CLAIMS

What is claimed is.

1. An electroplating composition comprising:

copper;

at least one acid, selected from sulfuric, methane sulfonic, amidosulfuric, aminoacetic, fluoboric, and mixtures thereof;

at least one halogen;

at least one additive, selected from an accelerating agent, a suppressing agent, and an accelerating-suppressing agent; and

the solution and mixture products thereof.

2. The aqueous electroplating composition according to claim 1, wherein the at least one additive consists of an accelerating agent and a suppressing agent.

3. The aqueous electroplating composition according to claim 1, wherein the at least one additive consists of an accelerating agent and an accelerating-suppressing agent.

4. The aqueous electroplating composition according to claim 1, wherein the at least one additive consists of a suppressing agent and an accelerating-suppressing agent.

5. The aqueous electroplating composition according to claim 1, wherein the accelerating agent is selected from a disulfide organic compound, a monosulfide organic compound, and mixtures thereof.

6. The aqueous electroplating composition according to claim 1, wherein the accelerating agent is provided in a concentration range from about 2 micromole/liter to about 500 micromole/liter.

7. The aqueous electroplating composition according to claim 1, wherein the accelerating agent comprises 1-propane sulfonic acid, and 3,3'-dithio-bis di-sodium salt.

8. The aqueous electroplating composition according to claim 1, wherein the accelerating agent comprises 1-propane sulfonic acid, 3-[(ethoxy-thiomethyl)thio], - potassium salt..

9. The aqueous electroplating composition according to claim 1, wherein the accelerating agent comprises (O-Ethyldithiocarbonato)-S-(3-sulfopropyl)-ester, potassium salt.

10. The aqueous electroplating composition according to claim 1, wherein the accelerating agent comprises a phosphonated disulfide.

11. The aqueous electroplating composition according to claim 1, wherein the accelerating agent is selected from a sulphonated monosulfide and a phosphonated monosulfide.

12. The aqueous electroplating composition according to claim 1, wherein the accelerating agent is selected from 3-mercapto-1-propanesulfonic acid and 2-mercaptoethanesulfonic acid sodium salt.

13. The aqueous electroplating composition according to claim 1, wherein the suppressing agent is provided in a concentration range from about 0.6 micromole/liter to about 600 micromole/liter.

14. The aqueous electroplating composition according to claim 1, wherein the suppressing agent is selected from at least one of a polyether, polyethylene glycol, polypropylene glycol, polyoxyethylene lauryl ether, polyethynene oxide, alkoxylated beta-naphtol, alkyl naphthalene sulphonate, polyimines, poly amines, and polyamids.

15. The aqueous electroplating composition according to claim 1, wherein the suppressing agent comprises a beta-naphtol having the structure:

$C_6H_4C_6H_3$-O-$(CH_2CH_3CH_2O)$n-$(CH_2$-$CH_2O)$m-H,

wherein n may be equal to 1 and wherein m may be equal to 1, and wherein the molecular weight is in the range from about 800 to about 1,500.

16. The aqueous electroplating composition according to claim 1, wherein the suppressing agent comprises a cross-linked polyamide in a concentration range from about 0.6

μmole/liter to about 600 μmole/liter, and wherein the cross-linked polyamide has an average molecular weight in a range from about 2,000 to about 3,000 gram/mole.

17. The aqueous electroplating composition according to claim 1, wherein the accelerating-suppressing agent is provided in a concentration range from about 1 μmole/liter to about 500 μmole/liter.

18. The aqueous electroplating composition according to claim 1, wherein the accelerating-suppressing agent comprises 1-propanesulfonic acid, 3-[[(dimethylamino)-thioxomethyl]-, sodium salt..

19. A method of plating comprising:

providing aqueous electroplating composition, comprising:

copper;

at least one acid, selected from sulfuric, methane sulfonic, amidosulfuric, aminoacetic, fluoboric, and mixtures thereof;

at least one halogen ion;

at least one additive, selected from an accelerating agent, a suppressing agent, and an suppressing-accelerating agent; and

the solution and mixture products thereof

contacting a substrate with the plating composition; and

impressing a multi-step direct-current waveform potential upon the substrate, wherein the multi-step direct current waveform potential comprises a stepped changing current density.

20. The method of plating according to claim 19, wherein impressing a multi-step direct-current waveform potential upon the substrate further comprises:

applying a direct-current waveform potential upon the aqueous electroplating composition before contacting the substrate therewith.

21. The method of plating according to claim 19, wherein the method further comprises:

pre-treating the substrate with a composition selected from deionized water, distilled water, an acid, a base, a solvent, a reducing agent, and mixtures thereof.

22. The method of plating according to claim 19, wherein the contacting the substrate comprises rotating the substrate relative to the plating composition at a rate in a range from about 0 to about 500 rpm.

23. The method of plating according to claim 19, wherein contacting the substrate comprises supplying plating composition at a rate from about 3 L/min to about 60 L/min.

24. The method of plating according to claim 19, wherein the plating composition is maintained in a temperature range from about 7 C to about 35 C.

25. The method of plating according to claim 19, wherein the multi-step direct current waveform potential comprises a stepped changing current density that comprises:

a nucleation current density; followed by

an initiation current density; followed by

at least one cycle of a fill current density that comprises a first forward pulse current density and a second reverse pulse current density; and followed by

a bulk fill current density.

26. The method of plating according to claim 19, wherein the multi-step direct current waveform potential comprises a stepped increasing current density that comprises:

a nucleation current density in a range from about 3 mA/cm^2 to about 70 mA/cm^2.

27. The method of plating according to claim 19, wherein the at least one cycle of a fill current density that comprises a first forward pulse current density and a second reverse pulse current density comprises cycles in the range from 1ns to about 1 min.

28. The method of plating according to claim 19, before contacting a substrate with the plating composition, the method further comprising:

forming a seed layer comprising copper upon the substrate, wherein forming a seed layer is selected from physical vapor deposition and chemical vapor deposition.

29. An article comprising:

a substrate containing a recess therein, wherein the recess has a characteristic width in a range from about 0.02 microns to about 100 microns,; and

a copper conductor in the recess, wherein the copper conductor has a grain size in a range from about 5 nm to about 100 nm.

30. The contact according to claim 29, wherein the recess has an aspect ratio in a range from about 1:1 to about 10:1.

31. The contact according to claim 29, wherein the grain originates from a <111> crystal configuration.

32. The contact according to claim 29, wherein the grain originates from a <200> crystal configuration.